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Antifouling paint.

An antifouling paint which can retain antifouling properties over a long period of time comprises (A) 100 parts by weight of a film-forming resin, and (B) 1-50 parts by weight of a chain organopolysiloxane containing oxyalkylene groups and having an HLB of 3-12.

This invention concerns an antifouling paint for application to underwater or marine structures including fishing nets such as stationary nets and culture nets, ocean tanks and bridge beams, various types of marine equipment, and ships; and in particular concerns an antifouling paint suitable for application to fishing nets.

Fishing nets and marine structures, marine equipment and ships are exposed to long periods of use in water and especially sea water. As a result of this, marine organisms tend to adhere to and proliferate on parts in contact with sea water, and the function of said fishing nets and other equipment may be impaired.

Insofar as concerns fishing nets, stationary nets and culture nets are left in sea water for very long periods of time. Adhesion and proliferation of marine organisms on these nets is particularly serious, so the nets must be replaced frequently and high economic losses are sustained. It is therefore essential to paint these fishing nets with an antifouling paint which makes it difficult for marine organisms to adhere to them.

The marine organisms referred to here which cause such a problem include animal species such as barnacles, hydrozoa, slimy sea squirts, sponges, small polyzoans, skeleton shrimps, hairy polyzoans, sea squirts, serpulids, sea anemones and oysters, and plant species such as sea lettuces, ceramium and green laver. It is also necessary to prevent the adhesion of organic waste or slime originating from the excreta or carcasses of these animal and plant species.

Antifouling paints with addition of silicone oils have been used for this purpose, conventional examples of these silicone oils being dimethyl silicone oil and phenylmodified silicone oil which has improved compatibility with the resin component and chemical components of the paint. However, although these conventional silicone oils conferred satisfactory water repellent properties on the paint, their antifouling properties were not so good, and an effective antifouling paint could not therefore be obtained. In conventional antifouling paints, moreover, it was unclear what kind of structure and properties the added silicone oil should have in order to confer good antifouling properties on the resin, and in particular acrylic resin, which is the main component of the paint film. A satisfactory antifouling paint therefore had still not been proposed.

The inventors of the present invention carried out an extensive investigation of the factors affecting the performance of antifouling paints with added silicone oil, and made the following observations:

(1) An organopolysiloxane with suitable coordination power to support the acrylic or other film-forming resin is required.

(2) An organopolysiloxane with intermediate hydrophilic properties with respect to the film-forming resin is most desirable.

(3) If a film-forming resin and liquid resin are used in conjunction, it is desirable that this organopolysiloxane has no interaction with the groups responsible for the cohesive force of the resins.

The inventor of this invention then found that excellent results were obtained by the addition of polyether modified silicone oils with a specific hydrophilic lipophilic balance (HLB).

One object of this invention is therefore to provide an antifouling paint with added silicone oil which retains high antifouling properties over a long period of time.

A further object of this invention is to provide an antifouling paint which is particularly effective when applied to fishing nets.

The above objects are attained by an antifouling paint comprising:

(A) 100 parts by weight of a film-forming resin, and

(B) 1-50 parts by weight of a chain organopolysiloxane containing oxyalkylene groups and having an HLB of 3-12.

The antifouling paint of this invention exhibits equivalent or better antifouling properties than conventional antifouling paints even if the blending proportion of antifouling agent is greatly reduced, and also retains these properties over a long period of time.

It is therefore an effective paint for underwater marine uses, and particularly for application to fishing nets.

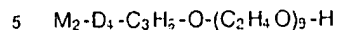
The above mentioned film-forming resin which is component (A) of this invention may be an "insoluble matrix type" resin or an ordinary organic polymer resin for use in antifouling paint. Examples of such insoluble matrix type resins are styrene-butadiene or vinyl chloride resins. Examples of organic polymer resins are polymers and copolymers of acrylic or methacrylic esters, styrene, vinyl acetate, monoethylene type unsaturated compounds such as ethylene and propylene, polyurethane, polyester and epoxy resins, urea resins, alkyd resins, and derivatives of these resins. There is no particular restriction on the molecular weight of the resin provided that it is high enough to effectively maintain strength.

Of these resins, acrylic resins are particularly effective as component (A).

The before mentioned chain organopolysiloxane with oxyalkylene groups which is component (B) of this invention is normally a polyether modified silicone oil, but it must in particular have a hydrophilic lipophilic

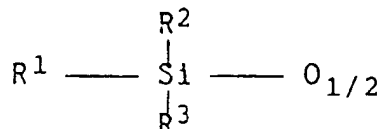
balance (referred to hereafter as HLB) in the range 3-12.

This component (B) may typically be an organopolysiloxane represented by the following general formula:



M is a monofunctional siloxane unit wherein one oxygen atom is bonded to a silicon atom, and is represented by the general formula:

10

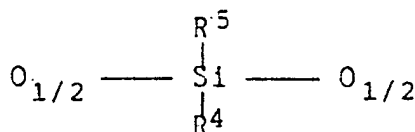


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where R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are alkyl groups, and usually methyl groups.

D is a bifunctional siloxane unit wherein 2 oxygen atoms are bonded to a silicon atom, and is represented by the general formula:

20



25

where R<sup>4</sup> and R<sup>5</sup> are alkyl, alkenyl or aryl groups, and are usually chosen from methyl, vinyl and phenyl.

As described above, HLB is the hydrophilic lipophilic balance. The HLB of high molecular weight compounds is generally given by the following formula:

30

$$35 \quad HLB = \frac{\text{Weight \% of polyoxyethylene in high molecular weight compound}}{5}$$

The hydrophilic properties of the compound are therefore greater for higher values of HLB.

As stated, the HLB of component (B) in this invention must lie within the range 3-12, but preferably within the range 4-11, and more preferably within the range 9-11. If HLB is less than 3, antifouling properties deteriorate, while if it is greater than 12, hydrophilic properties are too marked and the antifouling effect cannot be retained over a long period of time.

In addition to said components (A) and (B) of the antifouling paint of this invention, a liquid resin such as polybutene resin may also be included as a component (C), which confers adhesive properties on the paint (referred to hereafter as adhesive resin), and also functions to increase the pliancy of the film. Component (C) may for example be a random copolymer obtained by reacting, at low temperature in the presence of a catalyst, the isobutylene and normal butylene in the butane-butylene distillate produced by decomposition of naphtha. The blending proportion of component (C) may be adjusted suitably in order to provide film strength and retention of antifouling properties.

In particular, if the antifouling paint of this invention is used on underwater structures to prevent adhesion and proliferation of marine organisms, it is desirable that in addition to components (A), (B) and (C), it also contains an antifouling agent (D).

This antifouling agent may be a disinfectant or a repellent.

Said antifouling agent may be for example be an organotin compound, organozinc compound, halogenated aromatic compound, sulfamide type compound, or flakes or a fine powder of copper or cuprous oxide.

A photosynthesis inhibitor such as a triazine type compound may also be blended with the antifouling paint of this invention as a further component (E).

Conventional plasticizers, anti-drip agents, coloring pigments or body pigments known in the prior art may also be blended with the antifouling paint of this invention.

When incorporating (A), (B) and other components of this invention into the paint, they may first be diluted with an organic solvent such as toluene or xylene.

## EXAMPLES

We shall explain this invention in more detail with reference to specific Examples, but it should be understood that the invention is in no way limited by them.

The figures for blending proportions given in the tables are proportions by weight.

### EXAMPLES 1-5

Antifouling paints were prepared by blending and thoroughly dispersing the specified components by means of a Labo Mixer so as to obtain the compositions shown in Table 1.

The paints so prepared were applied to 35 cm x 45 cm fishing nets (Taito SeiKo K.K. "Hizex"(trade name), 400 denier, 60 strand, 60 mm mesh). After allowing the paint to harden, the nets were suspended off the coast of Shimonoseki, Yamaguchi Prefecture at an underwater depth of 2 m, and the adhesion of marine organisms and plants was observed so as to evaluate the antifouling performance of the paint. Table 3 shows the results.

### COMPARATIVE EXAMPLES 1-5

Components were blended so as to obtain the compositions shown in Table 2. Antifouling paints were prepared and their antifouling performance was evaluated in the same way as in Example 1-5. Table 3 shows the results.

TABLE 1

Blending Component		Example				
Component Type	Component Name	1	2	3	4	5
Film-forming resin	Acrylic resin *1	100	100	100	100	100
Chain organopolysiloxane containing oxyalkylene groups	Polyether modified silicone oil (HLB : 4) *2	—	—	—	—	22
	Polyether modified silicone oil (HLB : 10) *3	22	22	22	22	—
Adhesive resin	Polybutene resin *4	—	34	31	39	—
Antifouling agent	Triphenyltin chloride	—	—	—	26	—
Photosynthesis inhibitor	Ilgallol 1051 *5	—	—	6	15	—
Organic solvent	Xylene	285	364	371	471	285

(Note): \*1 Dai Nippon Inki Kagaku Kogyo K.K.: "Acrydic" 56-375 (trade name)  
 \*2~\*3 Shin-Etsu Kagaku Kogyo K.K.  
 \*4 Idemitsu Sekiyu Kagaku K.K.  
 \*5 Nippon Chiba Gaigi K.K.

TABLE 2

Blending Component		Comparative Example				
Component Type	Component Name	1	2	3	4	5
Film-forming resin	Acrylic resin *1	100	100	100	100	100
	Dimethyl silicone oil *2	22	—	—	—	—
Diorganopolysiloxane	Methylphenyl silicone oil *3	—	22	—	—	—
	Polyether modified silicone oil (HLB : 14) *4	—	—	22	—	—
Chain organopolysiloxane containing oxyalkylene groups	Polyether modified silicone oil (HLB : 0) *5	—	—	—	22	—
	Polybutene resin *6	—	—	—	—	39
Antifouling agent	Triphenyltin chloride	—	—	—	—	77
Photosynthesis inhibitor	Ilgallol 1051 *7	—	—	—	—	15
Organic solvent	Xylene	285	285	285	285	539

(Note): \*1 Dai Nippon Inki Kagaku Kogyo K.K.: "Acrylic" 56-375 (trade name)  
 \*2~\*5 Shin-Etsu Kagaku Kogyo K.K.  
 \*6 Idemitsu Sukiyo Kagaku K.K.

TABLE 3

(The figures in the Table indicate the surface area (%) of organisms covering the filaments of the net)

	One month		Two months		Three months		Four months		Five months		Six months	
	Animal	Plant	Animal	Plant	Animal	Plant	Animal	Plant	Animal	Plant	Animal	Plant
Example 1	1	0	5	0	12	0	20	1	25	3	25	4
Example 2	1 >	0	2	0	5	0	10	1	10	2	15	4
Example 3	1 >	0	1.5	0	3	0	5	1 >	10	1	10	2
Example 4	0	0	0	0	0	0	0	0	0	0	1	1 >
Example 5	1	0	8	0	20	0	30	1	40	3.5	40	4
Comparative Example 1	1	0	39	0	85	0	90	1	95	4	90	5
Comparative Example 2	1.5	0	16	0	70	0	85	1	85	4	90	5
Comparative Example 3	2.5	0	10	0	30	0	45	1	50	3	50	4
Comparative Example 4	1	0	16	0	65	0	75	1	85	4	85	4
Comparative Example 5	0	0	1 >	0	1	0	1 >	0	1	0	2	1 >

(Note) : Animal : Barnacles, serpulids, hairy polyzoans, sea squirts, slimy sea squirts.  
Mainly barnacles.

Plant : Ceramium, sea lettuce, thick-haired codium

The results of Table 3 show that antifouling paint of this invention is effective for marine applications, and in particular remarkably inhibits the adhesion of marine organisms to underwater structures.

## Claims

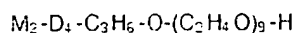
1. An antifouling paint comprising a film-forming resin and a silicone oil, characterised in that the paint comprises:

(A) 100 parts by weight of a film-forming resin, and

(B) 1-50 parts by weight of a chain organopolysiloxane containing oxyalkylene groups and having an HLB of 3-12.

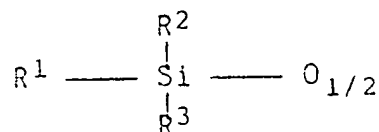
2. A paint as claimed in claim 1, wherein the film-forming resin (A) is an acrylic resin.

3. A paint as claimed in claim 1 or 2, wherein the chain organopolysiloxane (B) is represented by the following general formula:



in which M is a monofunctional siloxane unit containing one oxygen atom which is bonded to a silicon atom, and D is a bifunctional siloxane unit containing two oxygen atoms which are bonded to a silicon atom.

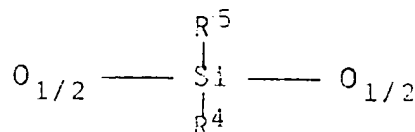
4. A paint as claimed in claim 3, wherein the unit M is represented by the following general formula:



in which  $R^1$ ,  $R^2$  and  $R^3$  are each an alkyl group.

5. A paint as claimed in claim 4, wherein one or more of  $R^1$ ,  $R^2$  and  $R^3$  are methyl groups.

6. A paint as claimed in claim 3 or 4, wherein the unit D is represented by the following general formula:



in which  $R^4$  and  $R^5$  are each an alkyl, alkenyl or aryl group.

7. A paint as claimed in claim 6, wherein  $R^4$  and  $R^5$  are selected from methyl, vinyl and phenyl groups.

8. A paint as claimed in any preceding claim, wherein the HLB lies within the range 4-11.

9. A paint as claimed in claim 8, wherein the HLB lies within the range 9-11.

10. A paint as claimed in any preceding claim, and further containing one or more components selected from adhesive resins, disinfectant anti-fouling agents, repellent anti-fouling agents, photosynthesis inhibitors, anti-drip agents, coloring pigments and body pigments.





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# EUROPEAN SEARCH REPORT

Application Number

EP 90 31 3598

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 537 985 (C.R. BOURIT) * Claim 1 * ---	1	C 09 D 5/14
A	DE-A-3 029 659 (GOSUDARSTVENNYJ NAUCNO-ISSLEDOVATELS'SKIJ I PROEKTNYJ INSTITUT LAKOKRASOCNOJ PROMYSLENNOSTI, MOSKVA, SU) * Claim 1; page 7, lines 10-21 * ---	1	
A	EP-A-0 287 505 (NIPPON OIL & FATS CO.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-07-1991	Examiner BEYSS E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

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